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Uranium(VI) Sorption and Diffusion in Montmorillonite and Bentonite: Experiments and Modeling

Ruth M. Tinnacher[1], Christophe Tournassat[2], James A. Davis[1]

[1)]Earth and Environmental Sciences Area, Lawrence Berkeley National Lab

[2)]BRGM, French Geological Survey, Orléans, France

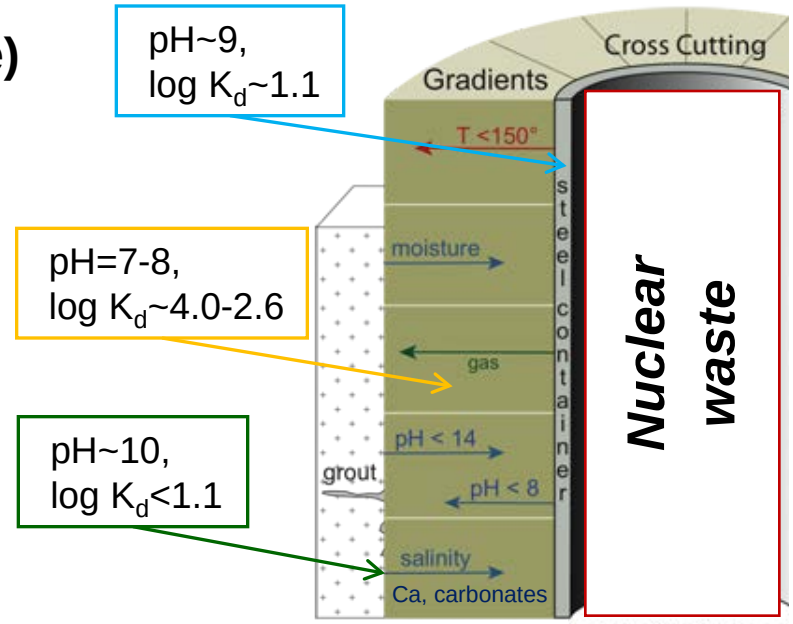
Used Fuel Disposition Campaign – Annual Meeting

Las Vegas, June 8 2016

Research Motivation

The long-term management of nuclear waste requires reliable predictions of radionuclide transport through engineered barrier systems (EBS).

- ⇨ **Compacted bentonite (montmorillonite)** is the proposed backfill material in EBS.
- ⇨ **Diffusion** will be the dominant transport mechanism in EBS that contributes to radionuclide dose in the environment.
- ⇨ **Gradients of chemical solution conditions and temperature** are expected over time and across EBS.

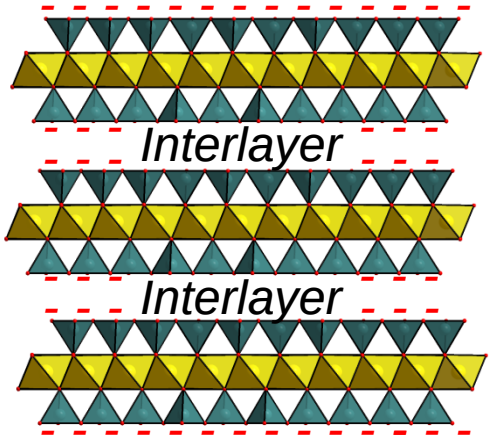


Goals:

- **Decrease the uncertainty** in actinide sorption / diffusion sub-models that are part of performance assessment models for waste repositories.
- **Investigate effects of changing chemical conditions and temperatures** on uranium(VI) sorption and diffusion.

System Complexities

Montmorillonite



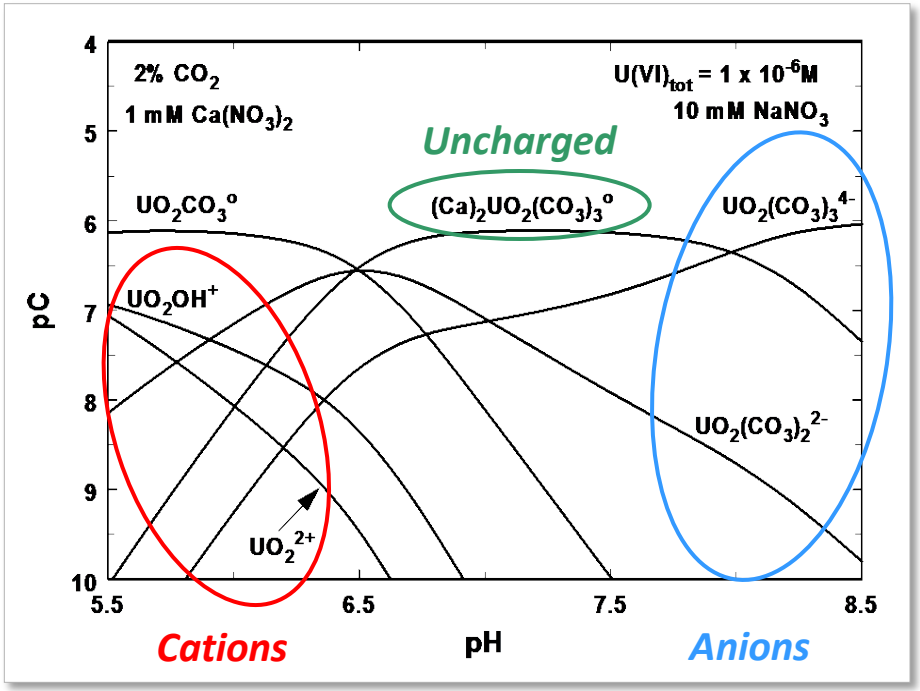
⇨ **Two sorption sites/surface reactions:**

- Cation exchange on basal surfaces
- Surface complexation on edge sites

⇨ **Two porosities/diffusion pathways:**

- Macropores between clay particles
- Small (1-3 nm) interlayer spaces within clay particles

Uranium(VI)



Uranium(VI) can be present as **cationic, anionic** or **neutral species** in solution.

System conditions affect sorption mechanisms and diffusion accessible porosities.

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Uranium(VI) Diffusion Experiments: Experimental Setup and Analysis

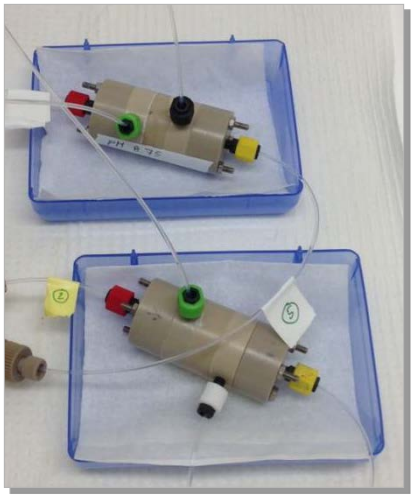
Experimental setup:

- Through-diffusion experiment
- Na-montmorillonite at 0.8 g/cm^3
- Solute: 2.35 µM $U(VI)_{Tot}$
- Target pH 8.75 or pH 8.95
- I=0.1 M NaCl/$NaHCO_3$
- Flow-rate: ~0.7 ml/min



Solution analysis to characterize:

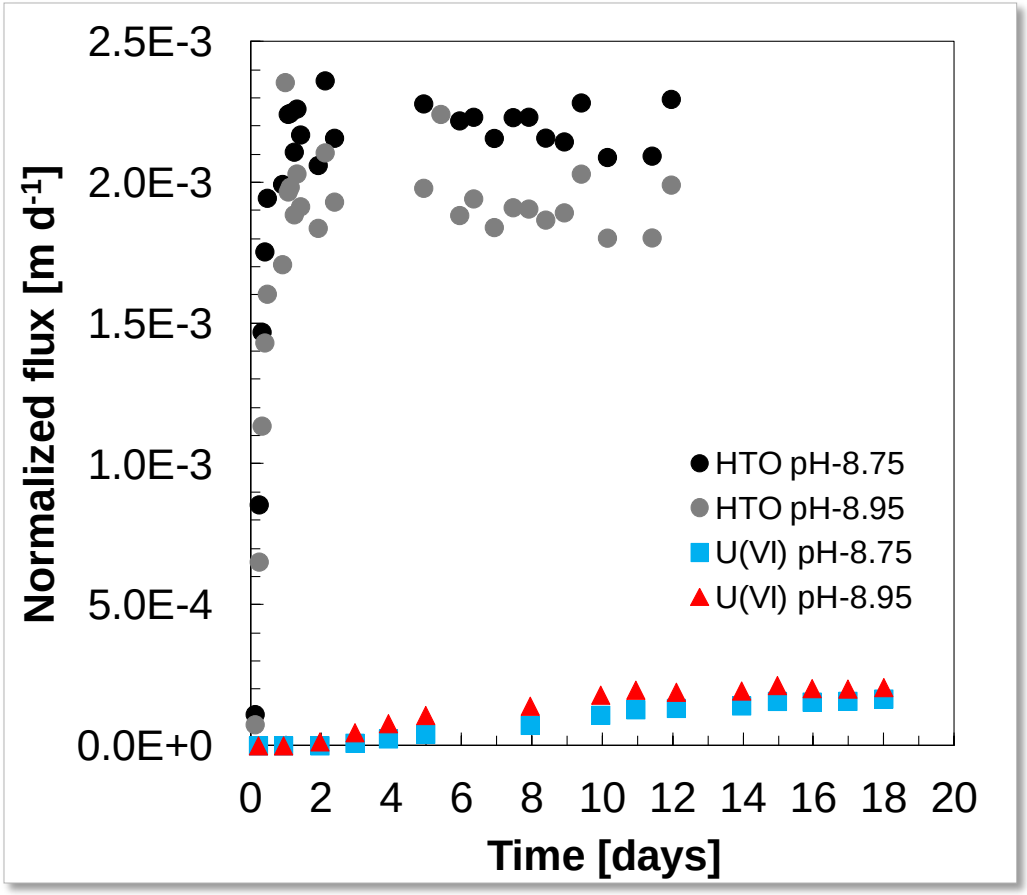
- U(VI) flux: U-233 (LSC)
- U(VI) speciation:
  - pH,
  - Ca, Fe, Si, Al, etc. (ICP-MS),
  - Total alkalinity (titrations)



Experimental steps:

- pH-equilibration of clay (batch): 3 weeks
- Saturation of dry, packed clay: ~3 ½ weeks
- Through-diffusion of HTO tracer: ~2 weeks
- Through-diffusion of U(VI): 11 weeks

Uranium(VI) Diffusion Experiments: Results



Experimentally-determined normalized flux (m d^{-1}):

$$J_i = \frac{C_{low}}{C_{high}} \frac{V_{low}}{A\Delta t}$$

Fick's 1st law:

$$J_i = -\varepsilon_{a,i} \frac{D_{w,i}}{G_i} \frac{dc_i}{dx}$$

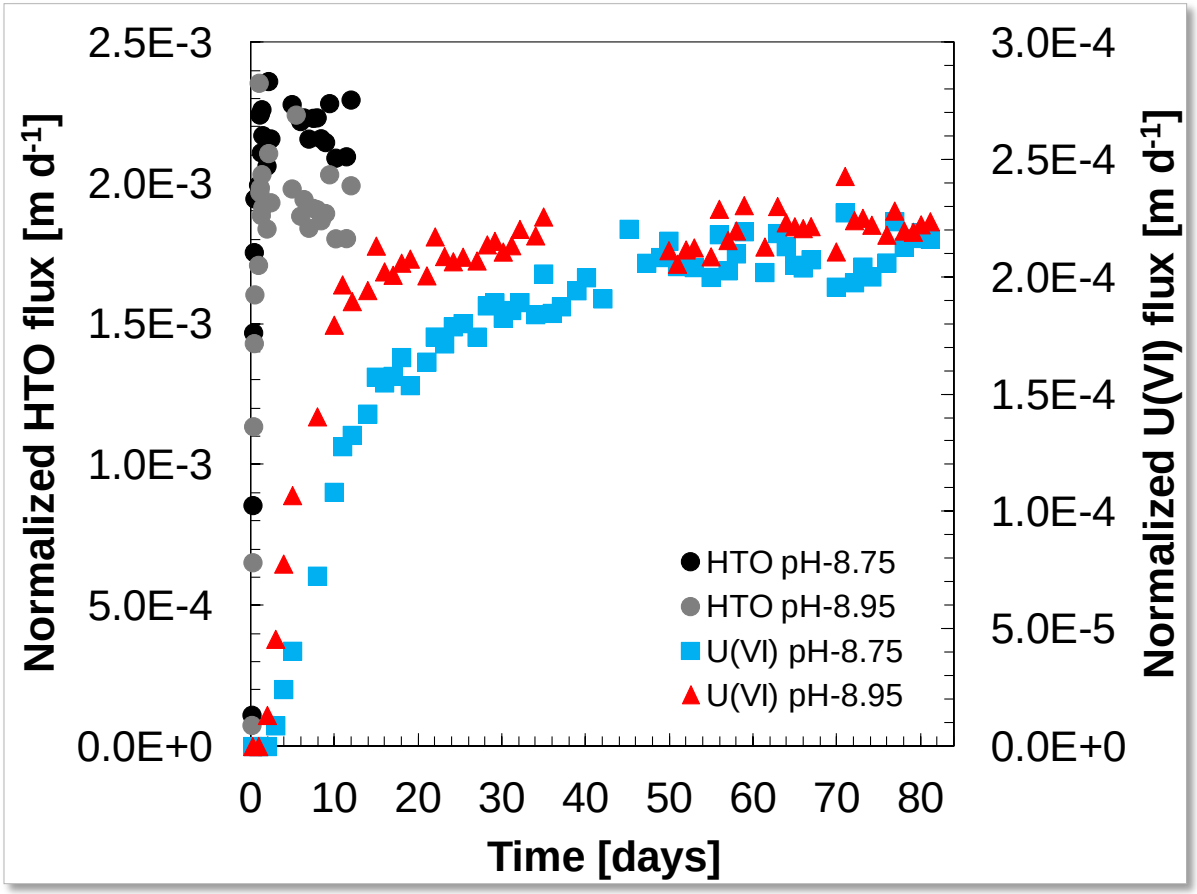
$\varepsilon_{a,i}$… *diffusion-accessible porosity*

G_i … *constructivity/(tortuosity)^2*

- Decrease in U(VI) flux relative to HTO flux.
- Indication for exclusion of anionic U(VI) species from clay interlayer spaces.

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Uranium(VI) Diffusion Experiments: Results



Estimated U(VI) K_d values:

- pH-8.75: 2.0 [L/kg]
- pH-8.95: 1.3 [L/kg]

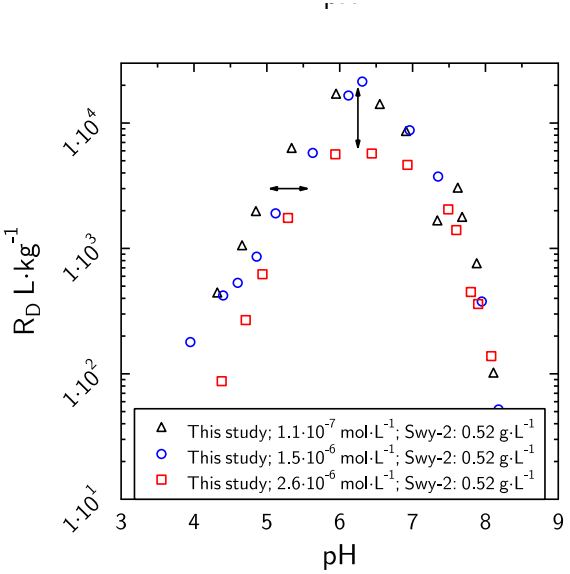
- Uranium(VI) retardation under both pH conditions: $K_{d,\ pH\text{-}8.75} > K_{d,\ pH\text{-}8.95}$.
- U(VI) sorption due to (strong) surface complexation, not (weak) cation exchange.
- Apparent kinetic limitations for U(VI) sorption at pH-8.75 relative to pH-8.95.

Summary: U(VI)-Montmorillonite Sorption Experiments

Experimental setup:

- 0.5 g/L Na-montmorillonite
- I = 0.1 M NaCl/$NaHCO_3$
- Sorption over: 48.5 hours
- Analysis of supernatant sol.:
  - pH
  - U-238
  - Total Inorganic Carbon (TIC)
  - Other metals: Ca, Mg, Si, Al, etc.

Experimental conditions:



Peculiarities of Montmorillonite Relevant for Development of Surface Complexation Models

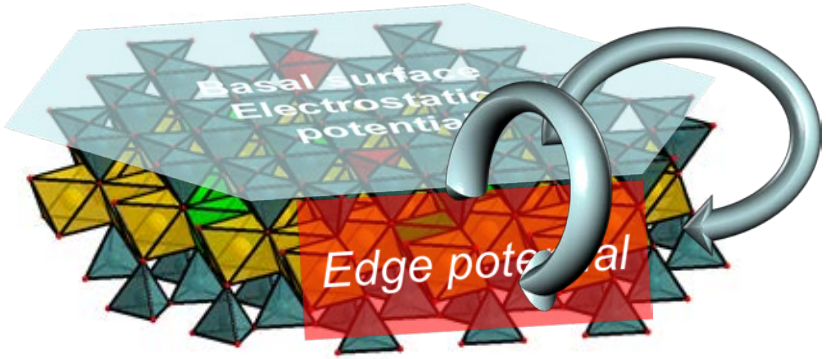
- Surface complexation models (SCMs) originally developed for simple mineral oxides.
- Metal surface complexation reaction:

$$> SOH + Me^{+} \leftrightarrow > SOMe + H^{+}$$

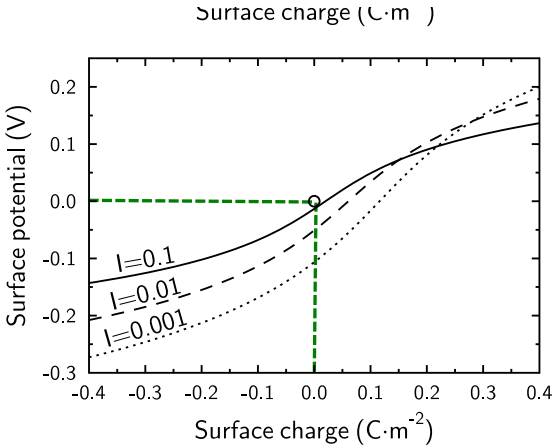
$$\Delta G_{tot} = \Delta G^{0}_{chem} + \Delta G^{0}_{coul}$$

$$K = \frac{[> SOMe](H^{+})}{[> SOH]} \exp\left(\frac{-F\psi}{RT}\right)$$

- Needed: Knowledge of surface potential as a function of pH, ionic strength, electrolyte
- For mineral oxides:
  Determine parameters based on potentiometric titrations of solid
- Montmorillonite: Spillover effect



H)(≡Al_{Oc}-OH_2)(≡$Si_T Al_{Oc}$O)



Montmorillonite

Setup: Surface Complexation Modeling

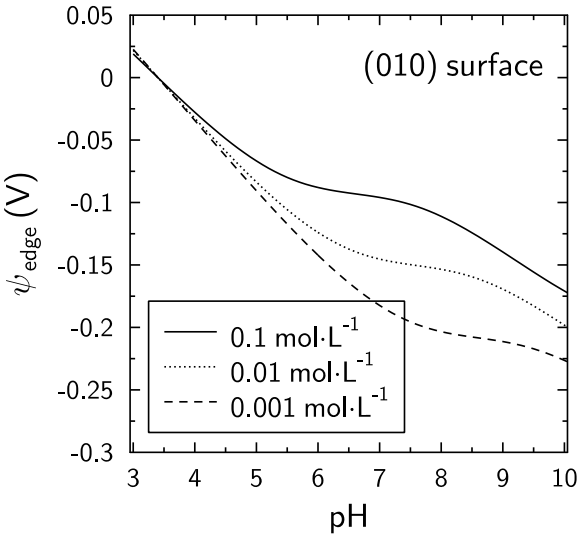
Surface model:

- Mean-field approach to describe relationship between surface charge and surface potential (Bourg, et al., 2007; Tournassat et al., 2013):

$$\frac{F\psi_{edge}}{RT} = A_1 a\sinh\left(A_2\left(Q_{edge} + A_3\right)\right)$$

A_1, A_2, A_3 *...fitted parameters, f(I)*

Q_{edge} *... surface charge of edge site*



- Protonation/deprotonation constants from first-principle molecular dynamics (Liu et al., 2015)

Uranium(VI) sorption:

- Modification of PHREEQC to include clay surface potential model.
- No ion exchange reactions considered due to high ionic strength in sorption experiments.
- Modeling steps:
  1. Fitting of surface complexation constants using U(VI) sorption data from 'CO_2-free' exp.
  2. Blind fit of U(VI) sorption under atmospheric P_{CO2}: This study and literature data
  3. Evaluation of relevance of ternary U(VI)-carbonato surface complexes

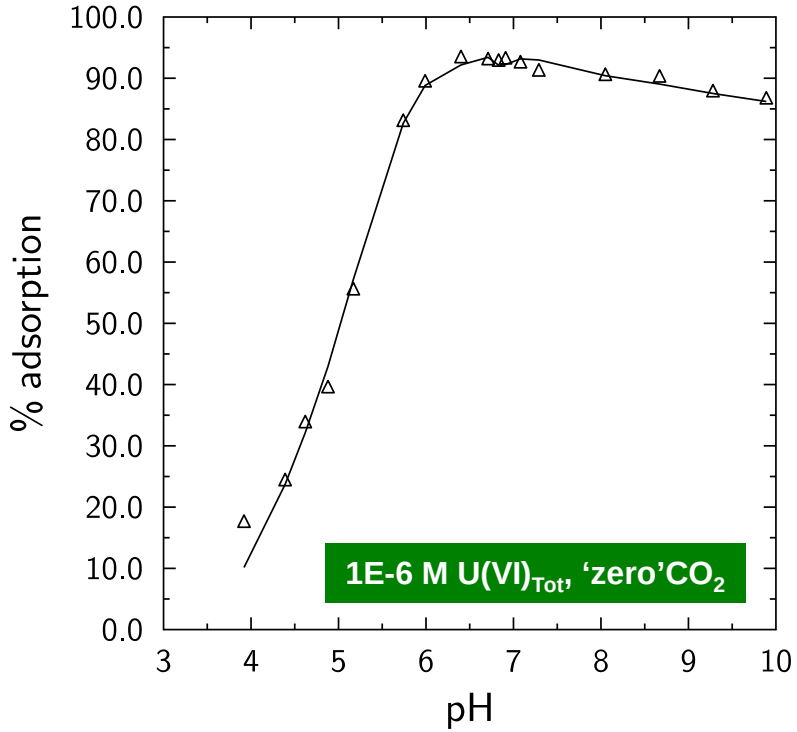
Results: Surface Complexation Modeling Step 1: Fitting of Complexation Constants

Step 1: **Fitting of surface complexation constants using U(VI) sorption data from 'CO$_2$-free' experiment only**

$>SOH_3 + UO_2^{+2} = >SOH_3UO_2^{+2}$ log K = 3.8

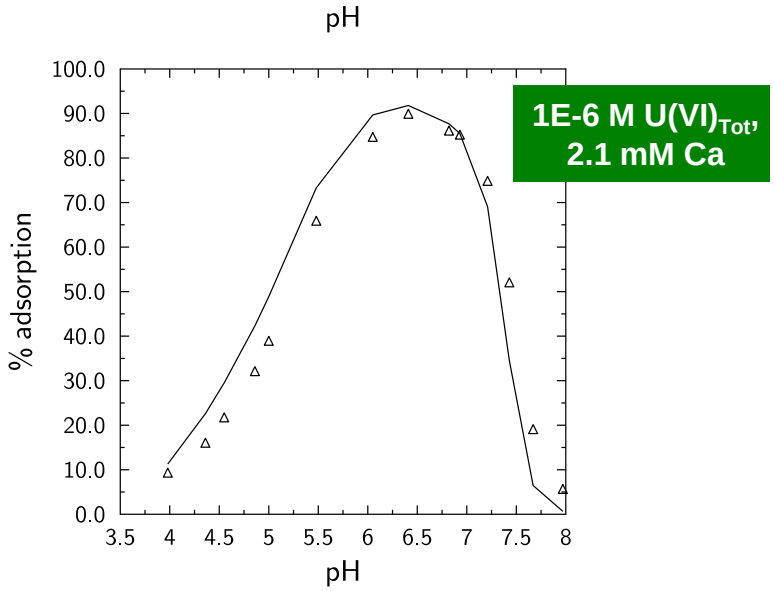
$>SOH_3 + UO_2^{+2} = >SOHUO_2 + 2\ H^+$ log K = -5

$>SOH_3 + UO_2^{+2} + 2\ H_2O = >SOUO_2(OH)_2^{-3} + 5\ H^+$ log K = -25.4

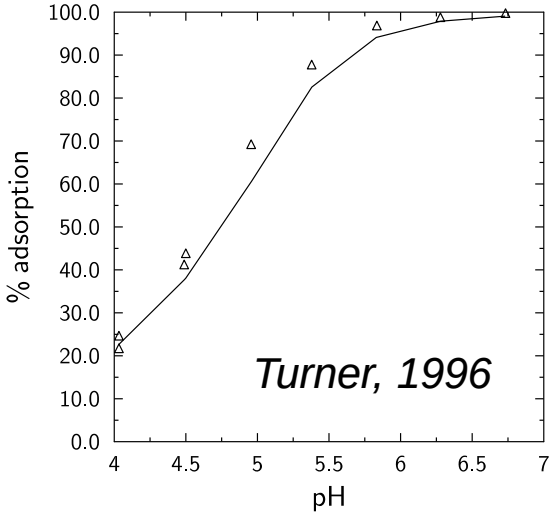


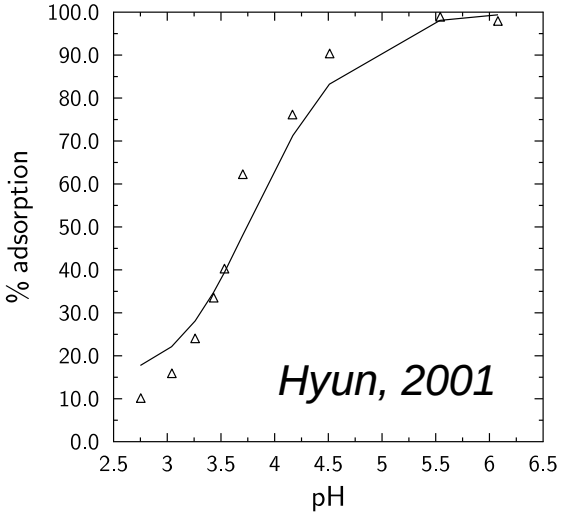
$>SOH_3$ edge site:
$(\equiv Si_T\text{-}OH)(\equiv Al_{Oc}\text{-}OH_2)(\equiv Si_T Al_{Oc} O)$

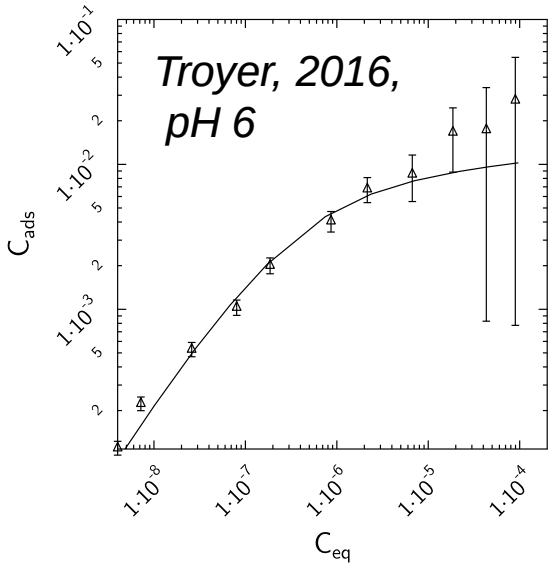
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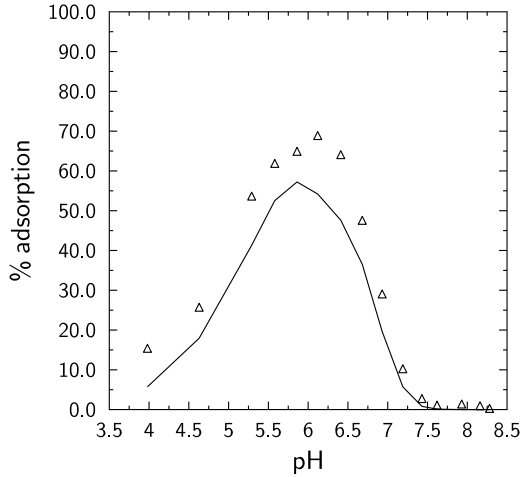
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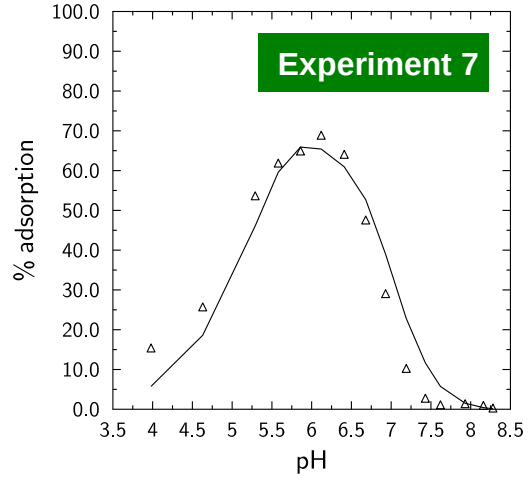






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by electrostatic SCM.

nate concentrations:

ufficient.

Summary: This Year's Accomplishments

Technical:

U(VI) diffusion: Completion of diffusion experiment in Na-montmorillonite at alkaline pH.

- ⇨ Uranium(VI) retardation due to sorption reactions.
- ⇨ First direct experimental evidence for U(VI) anion exclusion effects.

U(VI) sorption modeling:

Development of non-electrostatic and electrostatic SCMs for U(VI) sorption onto Na-montmorillonite.

- ⇨ Electrostatic SCM including "spillover" effect decreases number of fitting parameters needed (3 versus 10 surface complexes).
- ⇨ Formation of ternary U(VI)-carbonato surface complexes was not supported by electrostatic SCM.

Publications: *(UFD funded authors in **bold**)*

Tinnacher, R. M.; Holmboe, M.; Tournassat, C.; Bourg, I. C.; **Davis, J. A.** Ion Adsorption and Diffusion in Smectite Clay Barriers: Molecular, Pore, and Continuum Scale Views, *Geochimica et Cosmochimica Acta*, 2016, *177*, 130-149.

Gilbert, B.; Comolli, L. R.; **Tinnacher, R. M.**; Kunz, M.; Banfield, J. F. Formation and Restacking of Disordered Osmotic Hydrates of Smectite, *Clays and Clay Minerals*, 2015, *63*, 432-442.

Tournassat, C.; **Davis, J. A.**; Chiaberge, C. Modeling Acid/Base Properties at Montmorillonite Edge Surfaces. A review. To be submitted to *Environ. Sci. Technol.* in 2016.

Tinnacher, R. M.; Tournassat, C.; **Davis, J. A.** Modeling Uranium(VI) Sorption onto Montmorillonite: A Surface Complexation Model Accounting for the Spillover Effect on Edge Site Surface Potentials. To be submitted to *Geochim. Cosmochim. Acta* in 2016.

Conference Presentations:

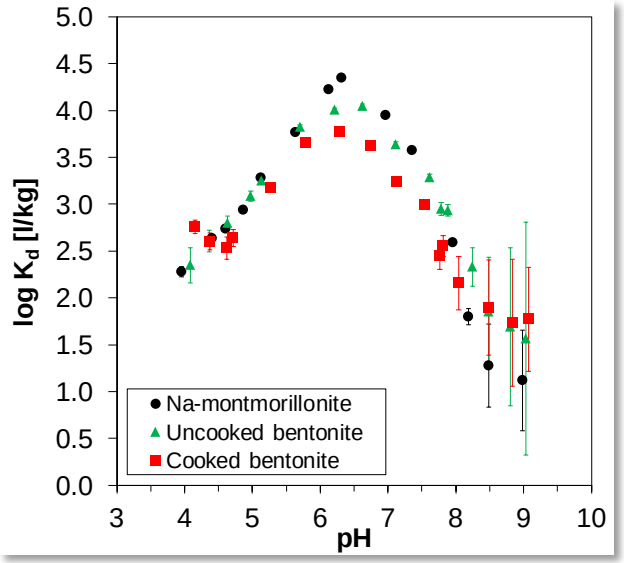
- *American Geophyiscal Union*, San Francisco, CA, December 2015.
- *American Chemical Society*, San Diego, CA, March 2016.
- *Colloque du Groupe Français des Argiles*, May 2016, Poitiers, France.

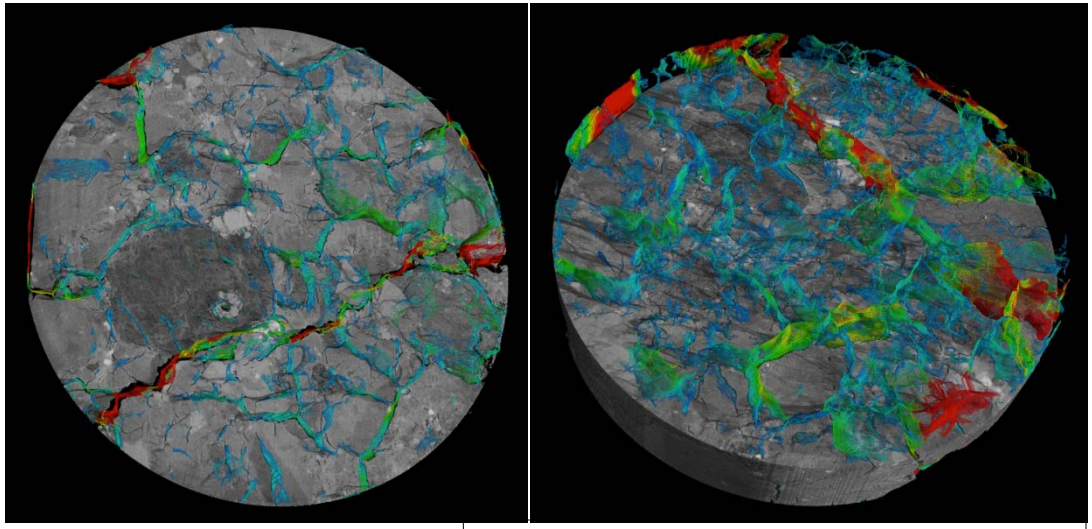
Outlook: Plans for Future Experiments Heat Effects and Increase in Solid Complexity

Motivation:

Potential changes in U(VI) sorption due to heat effects on bentonite

Microstructure characterization of FEBEX bentonite: Synchrotron X-ray microtomography (M. Voltolini, LBNL)





*BD 59-3 after heating at 120 °C for 8 min., 3.2 µm resolution, field of view ~6 mm, Fracture medial axes plotted in color, with increasing apertures from **blue** to **red***

Research Questions / Experimental Plans:

U(VI) sorption:

- Do U(VI) sorption affinities change after heat-treatment?
- Role of mineral 'impurities' for overall U(VI) sorption behavior?

U(VI) diffusion/mobility:

- Does fracture network alter overall U(VI) transport behavior (flux and breakthrough)?

Acknowledgements

Funding:

U.S. Department of Energy

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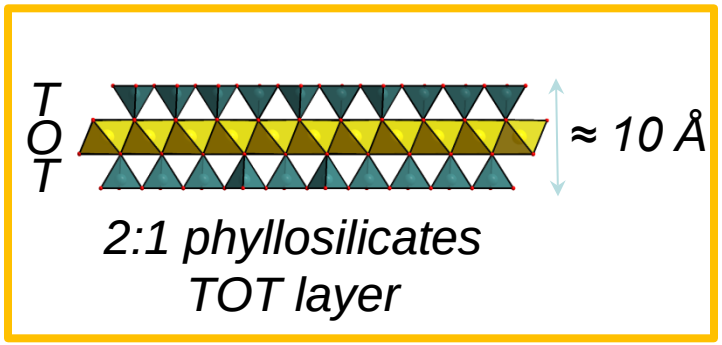
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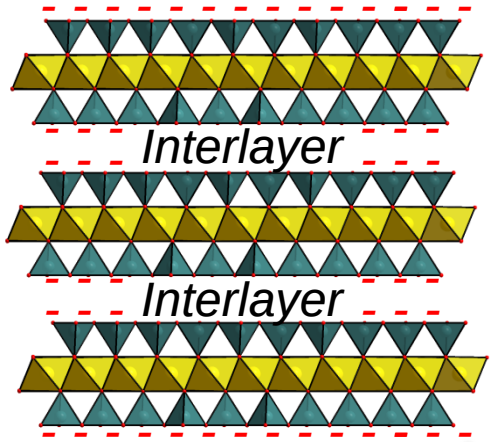


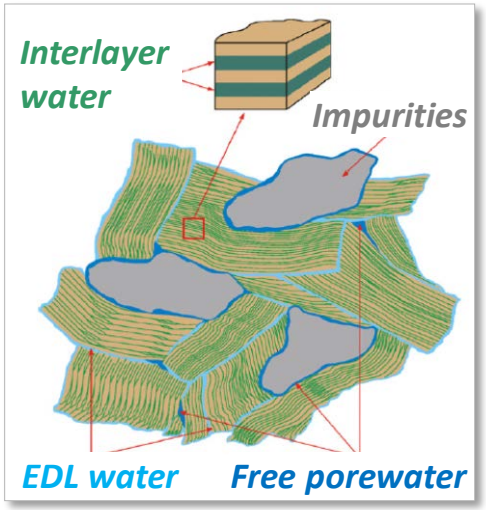


Additional slides

Structural complexity of Na-montmorillonite affects clay porosity







Tournassat and Appelo, 2011

Increasing scale ⇨

- **2 types of porosities and diffusion pathways due to clay structure:**
  - Small (1-3 nm) interlayer spaces within clay particles
  - Macropores between clay particles
- **System conditions affect diffusion-accessible porosities.**
- **Negative clay surface charges lead to:**
  - Cation sorption by ion exchange reactions
  - Potential exclusion of anions from interlayer spaces

Implications of System Complexities for Uranium(VI) Diffusion

Fick's 1st law:

$$J_i = -D_{a,i}\left(\varepsilon_{a,i} + \rho_b K_{d,i}\right)\frac{dc_i}{dx}$$

$D_{a,i}$ … *apparent diffusion coefficient*
$\varepsilon_{a,i}$ … *diffusion-accessible porosity*
ρ_b … *bulk density*
G_i … *constructivity/(tortuosity)^2*
$K_{d,i}$ … *sorption distribution coefficient*

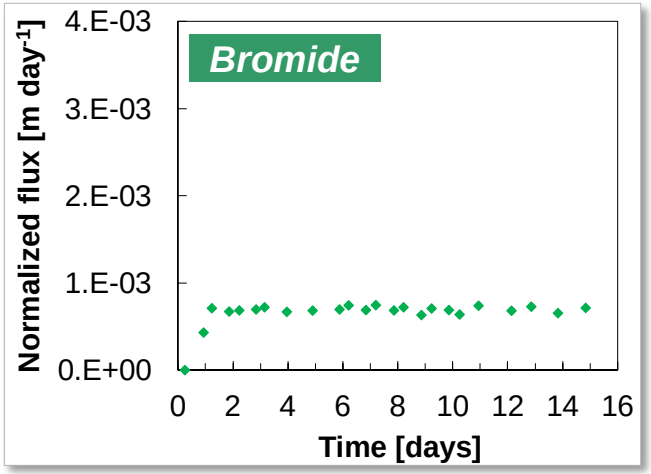
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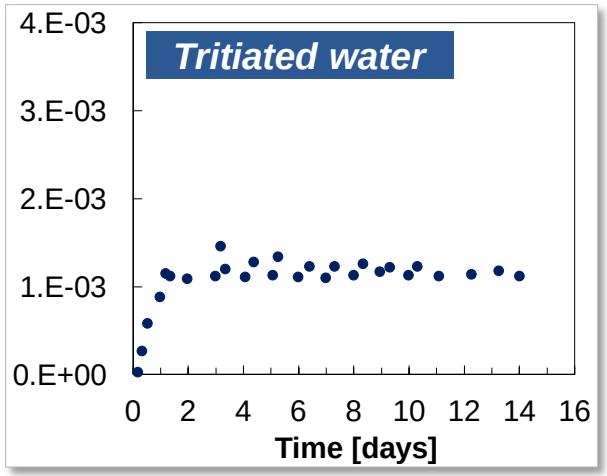
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$K_{d,i}$ … *sorption distribution coefficient*

Anion exclusion from interlayers





- Decrease in diffusion-accessible porosity
- Decrease in diffusive flux

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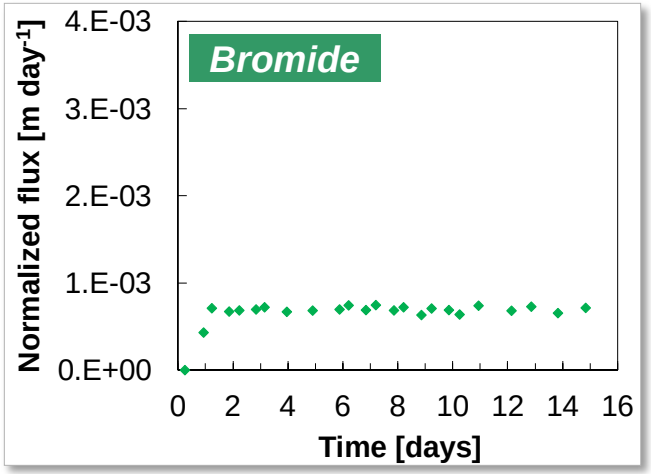
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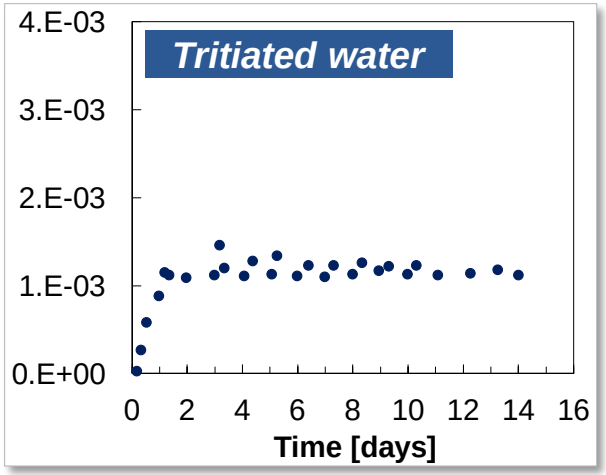
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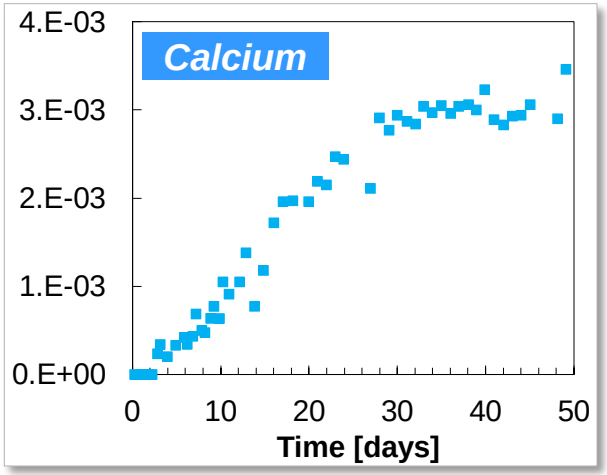
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Anion exclusion from interlayers ***Sorption reactions***





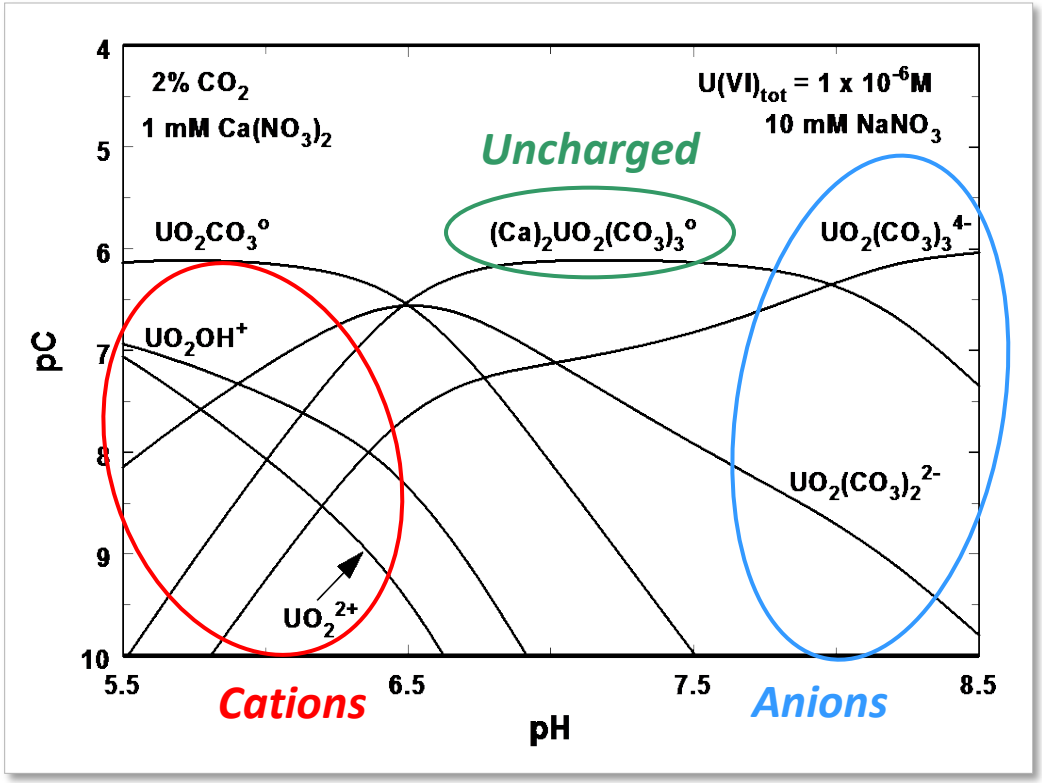


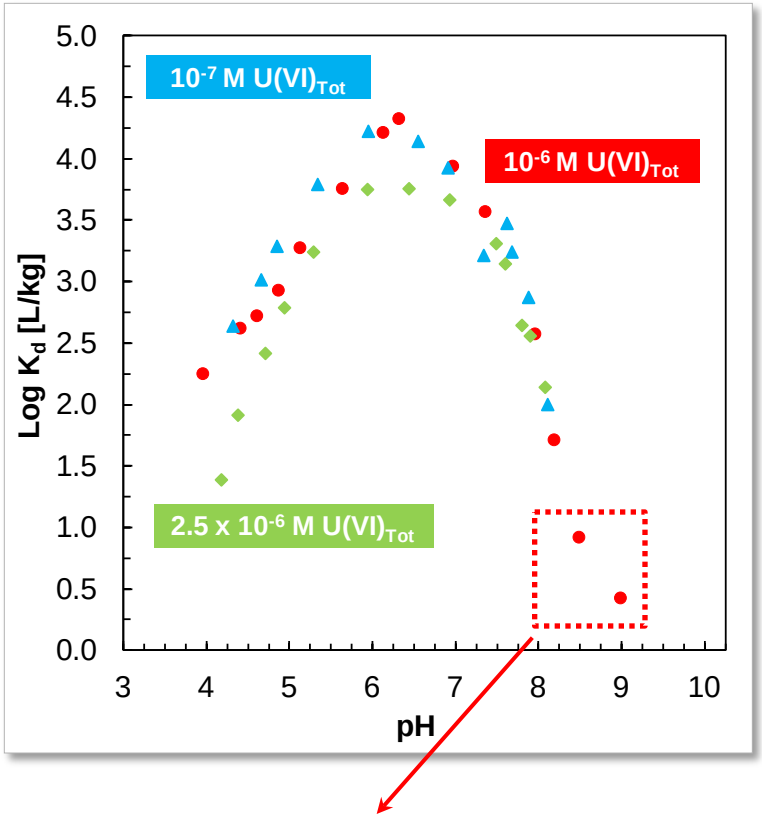
- Decrease in diffusion-accessible porosity
- Decrease in diffusive flux

- Retardation (cation exchange/surf. complex.)
- Weak sorption: Increase in flux
- Strong sorption: No change in flux

Uranium(VI) Diffusion experiments: Selection of pH Conditions

Goal: Evaluate effects of anion exclusion and uranium(VI) sorption reactions.





- Target range of log K_d values: 0.7-1 [L/kg] (K_d=5-10 [L/kg])
- Two parallel diffusion experiments at target pH values of pH=8.75 and pH=8.95.

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Uranium(VI) Diffusion Experiments: Experimental Setup and Analysis

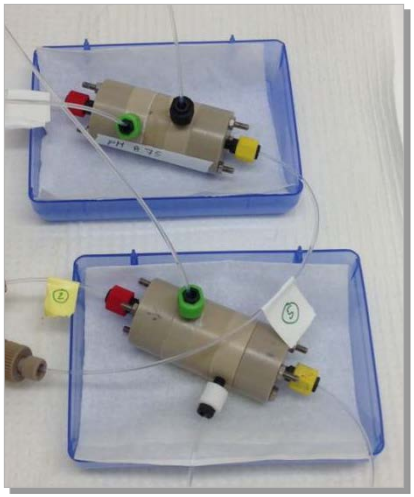
Experimental setup:

- Through-diffusion experiment
- Na-montmorillonite at 0.8 g/cm^3
- Solute: 2.35 µM $U(VI)_{Tot}$
- pH~8.69 or pH~8.87
- I=0.1 M NaCl/$NaHCO_3$
- Flow-rate: ~0.7 ml/min



Solution analysis to characterize:

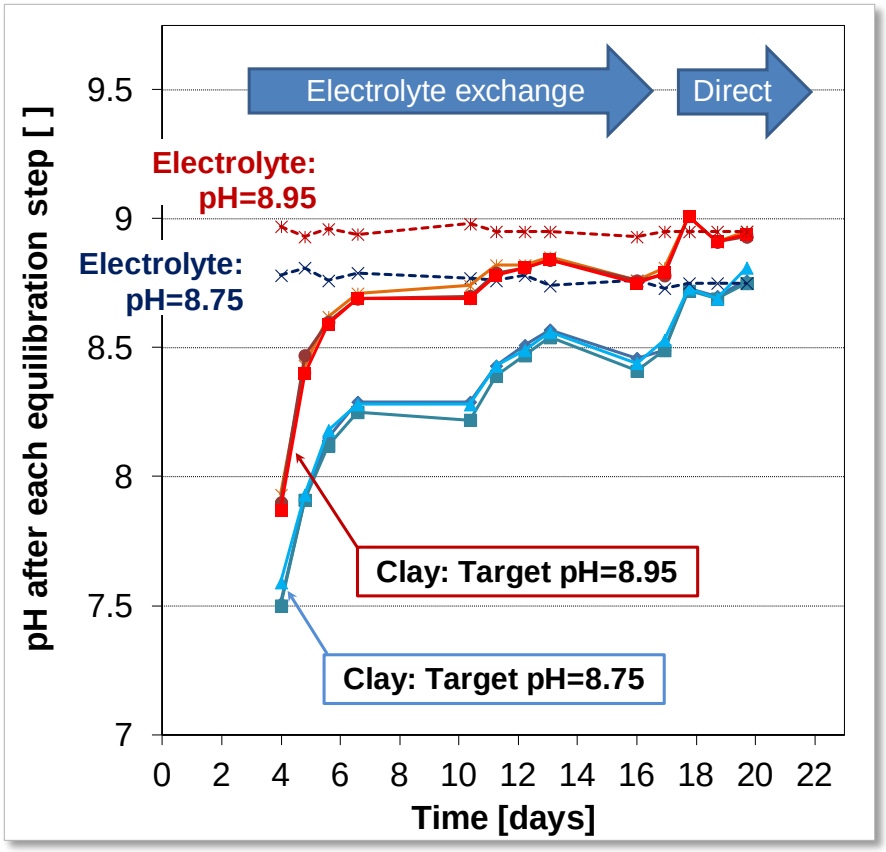
- U(VI) flux: U-233 (LSC)
- U(VI) speciation:
  - o pH,
  - o Ca, Fe, Si, Al, etc. (ICP-MS),
  - o Total alkalinity (titrations)

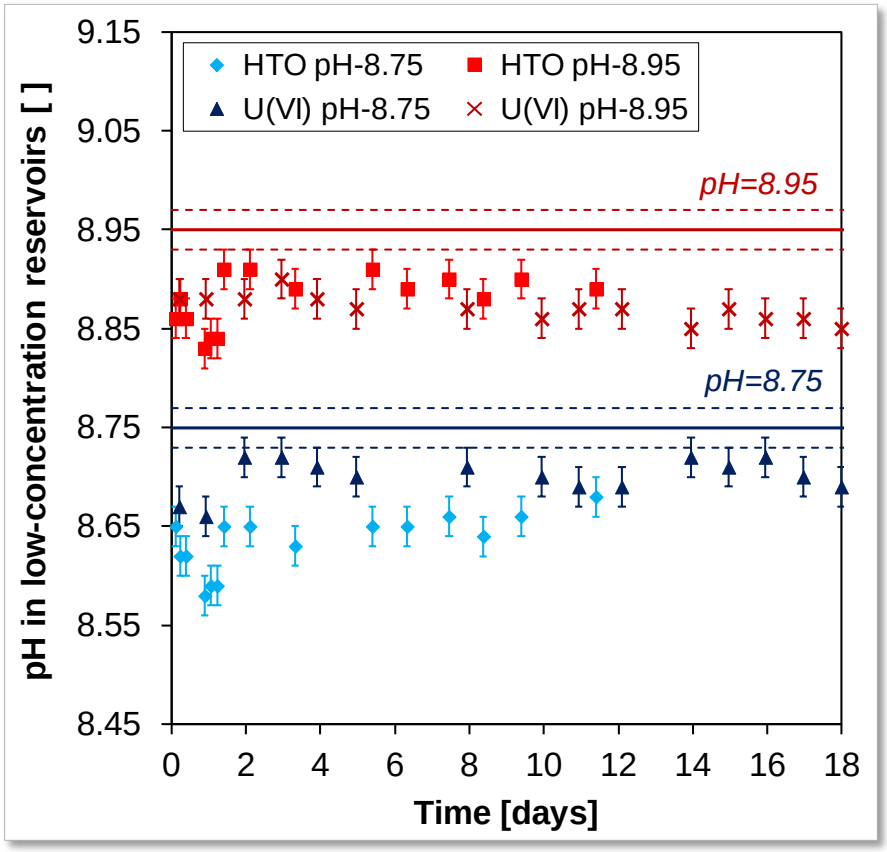


Experimental steps:

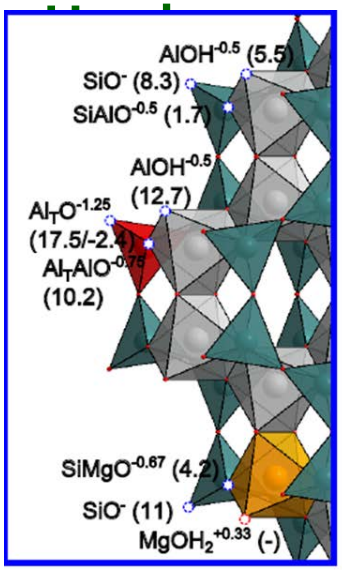
- pH-equilibration of clay (batch): 3 weeks
- Saturation of dry, packed clay: ~3 ½ weeks
- Through-diffusion of HTO tracer: ~2 weeks
- Through-diffusion of U(VI): 11 weeks

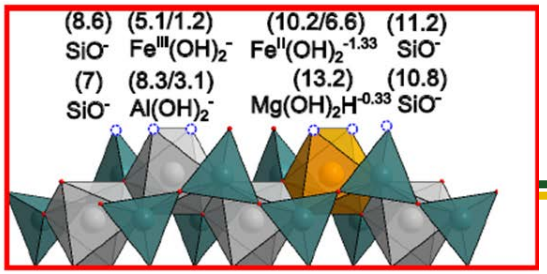
Uranium(VI) Diffusion Experiments: Equilibration of pH Conditions

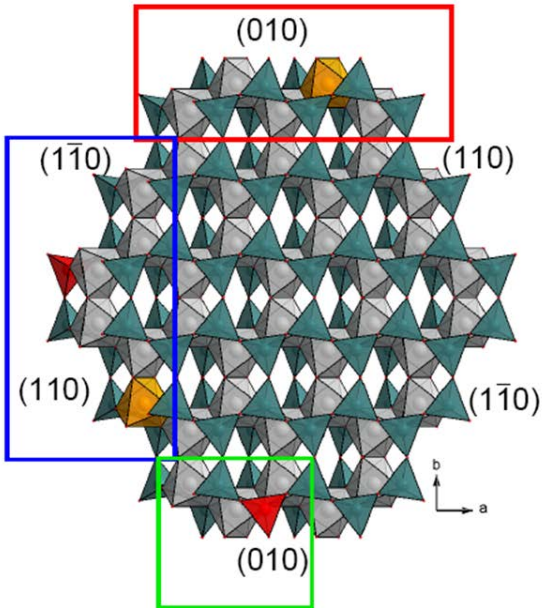


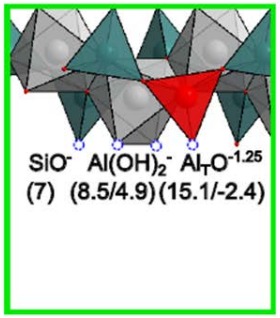


- Sufficiently stable pH conditions during diffusion experiments.
- Average pH drop less than 0.1 pH-units.



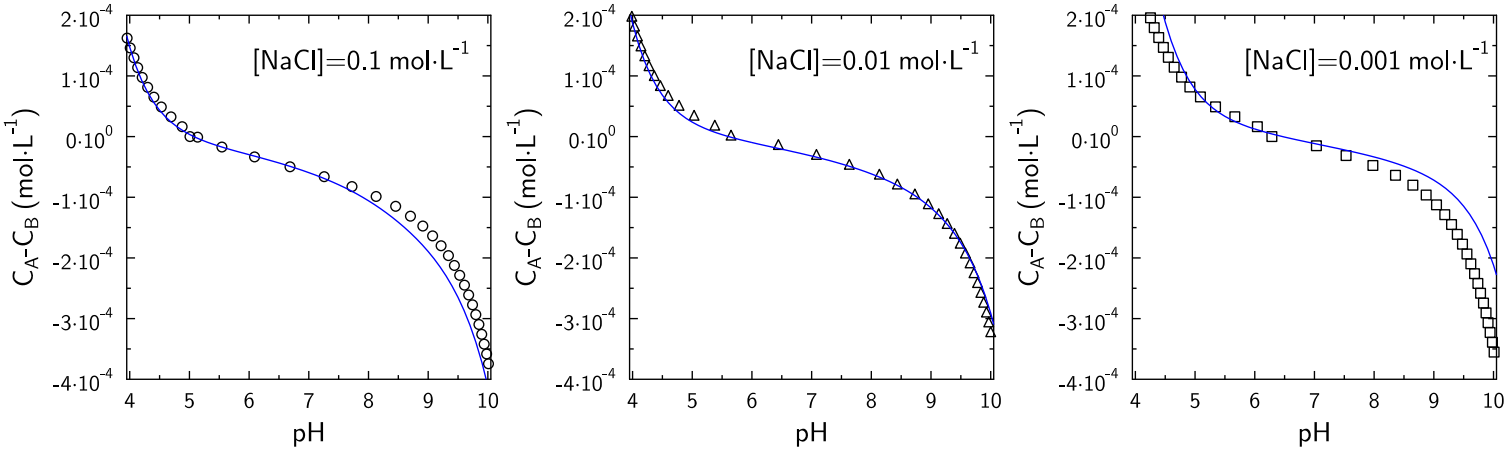




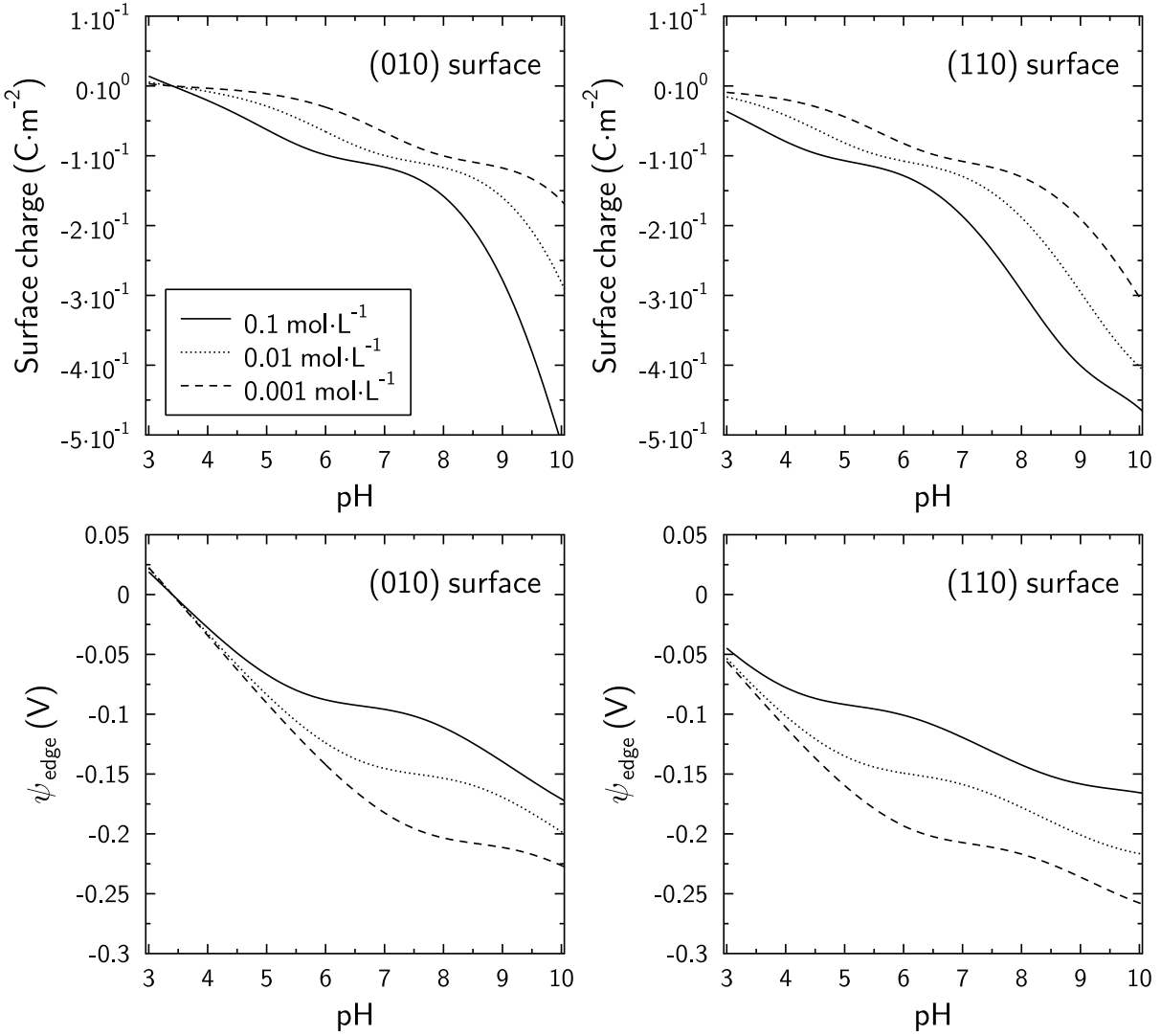


Protonation/deprotonatin constants from FPMD calculations (from literature)

Predicted titration curves vs. experimental data



Used Fuel Disposition



Predicted edge surface charge and potential as a function of pH for montmorillonite particles immersed in 0.001, 0.01, and 0.1 mol·L^{-1} NaCl background electrolyte.
Simulations were carried out with . $x_{>Si-Al-Si} = 1$

Evaluation of ternary U(VI)-carbonato surface complexes

$>SOH_3 + UO_2^{+2} + HCO_3^- = >SOH_3UO_2(CO_3) + H^+$ log K = 5

$>SOH_3 + UO_2^{+2} + 2\ HCO_3^- = >SOH_2UO_2(CO_3)_2^{-3} + 3\ H^+$ log K = -1.5

Adsorption model with only 3 (5) reactions in absence (presence) of U-CO3 complexes
For comparison the non-electrostatic model of Marques et al., 2012 has 10 surface complexes

→ *Better description of the system with fewer parameters*

In the presence of carbonate, model outcomes are very dependent on CO2 partial pressure
→ *It is necessary to measure this parameter to extract sorption constants for U sorption.*

Uranium(VI) Sorption Studies: Goals, Materials and Setup

Goals:

- Investigate potential impacts of heat-induced mineral alterations in bentonite on U(VI) sorption behavior.
- Provide input parameters for U(VI) diffusion models.

Solids:

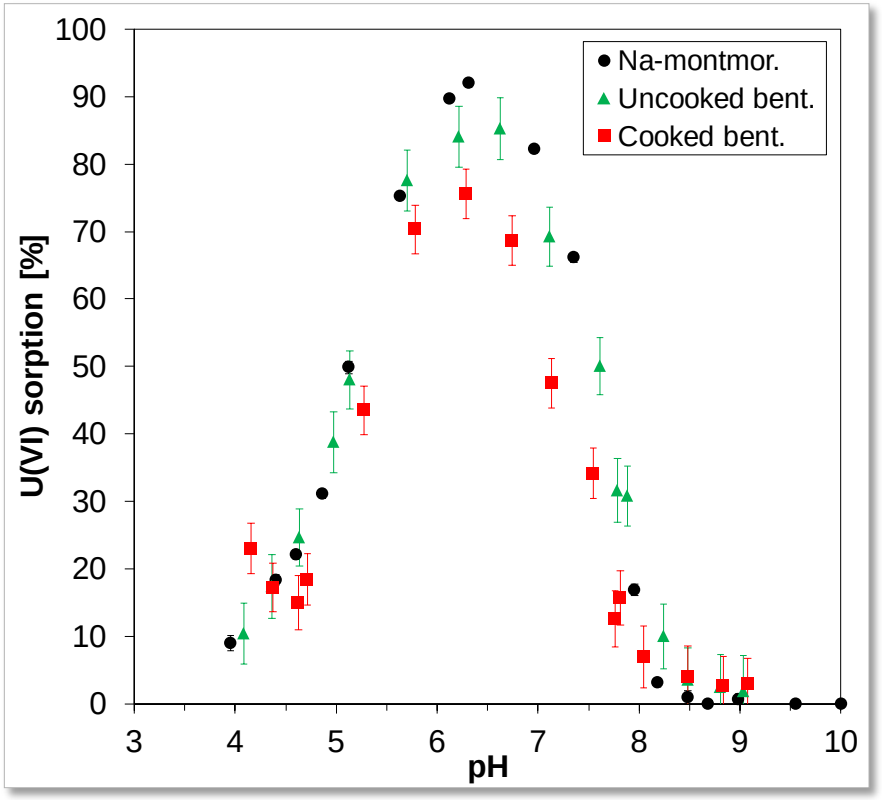
- 'Cooked' and 'uncooked' bentonite (EBS-12, LANL)
- Na-montmorillonite as reference (Swy-2, pretreated)

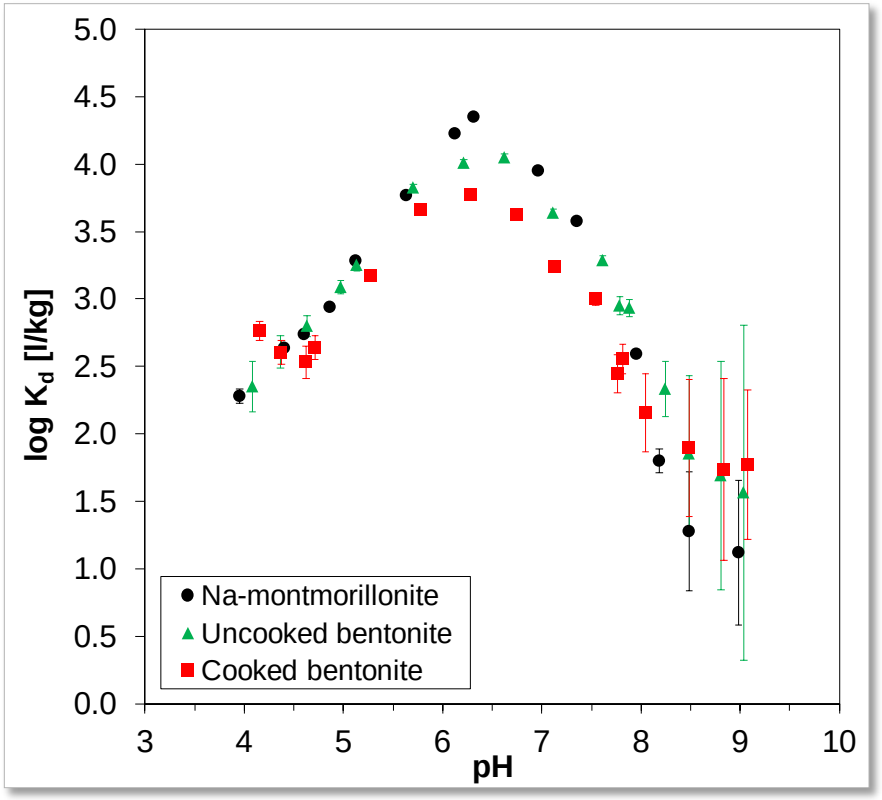
Experimental conditions:

- 0.5 g/L solid
- I = 0.1 M $NaCl/NaHCO_3$
- $U(VI)_{Tot}$: 10^{-6} mol/L (U-238)
- Atmospheric CO_2
- Time-dependent sampling over 21 days
- ICP-MS analysis for U-238 and Ca, Fe, Si, Al, etc. (ongoing)



Uranium(VI) Sorption Studies: 2-Day Sorption Data





Heat treatment leads to:

- Lower uranium(VI) sorption under circum-neutral pH conditions.